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To explore the nature of these light ↔ charges exchange processes in electronic polymers we have fabricated and evaluated bilayer photoreceptors and bilayer LEDs from conjugated polymers. The efficiencies and other performance characteristics of these devices are shown to depend on not only molecular structure and intrinsic properties of the materials but also on the "polymer device engineering" factors such as the polymer/polymer interfaces.

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EXCHANGING LIGHT AND CHARGES IN ELECTRONIC POLYMERS

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Abstract

Optoelectronic devices such as xerographic photoreceptors (PRs) and light emitting diodes (LEDs) represent two examples of promising applications of semiconducting polymers. In the former example, efficient generation of charge carriers from absorbed light is the central focus. In the latter examples, efficient generation of light from injected charges is the goal. To explore the nature of these light ↔ charges exchange processes in electronic polymers we have fabricated and evaluated bilayer photoreceptors and bilayer LEDs from conjugated polymers. The efficiencies and other performance characteristics of these devices are shown to depend on not only molecular structure and intrinsic properties of the materials but also on the "polymer device engineering" factors such as the polymer/polymer interfaces.

Introduction

Light emitting diodes (LEDs) fabricated from conjugated polymers, first demonstrated in 1990 (1), are currently of wide interest for applications such as indicators and flat panel displays (1-7). These polymer LEDs have the configuration of an injection electroluminescence (EL) cell in which an *active* electronic polymer (emitter) layer is sandwiched between two conductive electrodes. The most efficient polymer LEDs reported to date have EL efficiencies (photons/electron) of about 1-4% and consist of bilayer or multilayer arrangement of emitter and charge transport polymers (5). It is interesting to note that the typical operational electric fields in polymer LEDs is in the range of 10^5 to 5×10^6 V/cm which are similar to those found in xerographic photoreceptors (8-10).

Organic polymer-based photoconductive materials which are widely used as photoreceptors in electrophotographic imaging and laser printing represent the first major commercial application of electronic polymers (8). These organic photoreceptors are typically bilayer devices in which one layer serves as a charge generation layer (CGL) and the other serves as a charge transport layer (CTL). Current CTL materials are typically triarylanine molecules physically dispersed in a polymer matrix or covalently attached to polymers (8-10). Current CGL materials are also small molecules such as phthalocyanines, perylenes, squaraines, and azo compounds dispersed in polymers (8-10). We recently proposed to explore conjugated polymers as the charge generation materials in photoreceptors (9,10). We have found that bilayer photoreceptor devices also provide an opportunity to investigate charge transport and charge trapping processes of relevance to the development of conjugated polymer LEDs.

In this paper, we report the fabrication and evaluation of conjugated polymers-based photoreceptors and LEDs. The effects of polymer molecular and solid state structures as well as "polymer device engineering" factors on the efficiencies of light or charge generation in these devices will be explored. Of particular significance is our finding that charge transport and charge carrier range in conjugated polymers play critical roles in both the efficiency of charge photogeneration in photoreceptors and the efficiency of light emission in LEDs.

Experimental Approaches

Our studies of polymer optoelectronic devices have focused on conjugated rigid-rod polymers such as poly(p-phenylene benzobisthiazole) (PBZT), poly(2,5-pyridyl benzobisthiazole) (PPyBT), poly(2,6-(4-(phenyl) quinoline) (PPQ), and poly(benzimidazobenzophenanthroline ladder) (BBL). The molecular structures of some of these conjugated polymers are shown in Figure 1.

The bilayer photoreceptor devices shown in Figure 2 were fabricated by spin coating of solutions of the polymers. Poly(ethylene terephthalate) (PET) substrates (5 x 5 cm^2) overcoated with evaporated nickel (Ni) were used to deposit thin films (~10-1000 nm) of conjugated polymers by spin coating. Deposition of optical quality thin films of these and other conjugated polymers from their organic solvent (e.g. nitromethane) soluble Lewis acid ($GaCl_3$, $AlCl_3$, etc) coordination complexes have previously been reported by our laboratory (10,11). The resulting vacuum dried (6 hr, 80°C) samples were next blade coated with a polycarbonane (PC) solution containing tris (p-tolyl) amine (TTA) in dichloromethane (18-20 wt % total solids). The resulting TTA/PC films (10-25 μm thick) served as the charge transport layer. The successful preparation of these bilayer photoreceptor devices was due to the insolubility of the conjugated polymers in dichloromethane.

Both single-layer and bilayer LEDs were fabricated starting with indium-tin-oxide (ITO) coated glass substrates. The polymer thin films were spin coated onto the ITO coated

glass substrates. Aluminum was used as the electron-injecting electrode and was evaporated onto the polymer thin films at a vacuum pressure of 10^{-5} torr. The thickness of the Al electrode was 100-130 nm. The resulting polymer LEDs had the configuration Al/polymer/ITO in the case of the single layer devices. The bilayer LEDs shown in Figure 3 were similarly fabricated, resulting in a device structure of the type Al/polymer 1/polymer 2/ITO. The polymer layer adjacent to the Al electrode was envisioned to be an electron-transporting material as is the case with those in Figure 1 (12). The polymer layer adjacent to the ITO was expected to be a hole-transporting material. We have explored the TTA/PC used in the bilayer photoreceptors as well as poly(N-vinyl carbazole) (PVK) and poly(p-phenylene vinylene) (PPV) as hole-transporting materials in LEDs.

Characterization of the bilayer photoreceptor devices, especially the electric field dependent quantum efficiency for charge photogeneration, has been done primarily by the xerographic photoinduced discharge technique (9,10). Our experimental system for these measurements as well as the computer data acquisition and analysis have previously been described (10). Electroluminescence (EL) spectra of the LEDs were obtained by using a calibrated Photo Research model PR-60 colorimeter. The LED brightness was measured by using a silicon avalanche photodiode. The EL quantum efficiency (photons/electron) was estimated by using reported techniques (4-6).

Results and Discussion

We will first present the results for the bilayer photoreceptor of Figure 2. The typical photoinduced discharge curve (PIDC) for a photoreceptor using a conjugated polymer CGL is exemplified by that for PPyBT shown in Figure 4A. This PIDC for PPyBT was obtained with 470 nm illumination which is near the absorption maximum of the polymer. The photon energy required to discharge the surface potential to half its original value is known as the photosensitivity ($E_{1/2}$) and was found to be 9 ergs/cm^2 for PPyBT. On the other hand the dark decay was about 10 V/s. These properties compare favorably with many current photoreceptors (13). Similar PIDC data for PBZT and BBL, for example, showed that the photosensitivity and dark decay were 12 and 18 ergs/cm^2 and 0.4 and 0.2 V/s, respectively.

The quantum efficiency for charge photogeneration $\phi(E)$ was determined from the initial rate of photodischarge in the PIDC data for various bilayer devices. A typical example is shown in Figure 4B for a photoreceptor containing a PPyBT CGL. The quantum efficiency increases from ~1% at about 6 x 10^5 V/cm to ~50% at ~10^6 V/cm. Similar results for other conjugated polymers show that the efficiency for photogeneration of charge carriers varies dramatically with molecular structure. For example the high field (~10^6 V/cm) quantum efficiency for PBZT and BBL are ~ 32% and 20% respectively. Furthermore, for each fixed conjugated polymer we found that the measured quantum efficiency also depends on thickness of the charge generation layer. This implies that there is some charge trapping in the thicker conjugated polymer layers. In contrast, the thickness of the charge transport layer had no effect on the measured quantum efficiency. This confirms the fact that the TTA/PC layer is a trap-free material as is well known in the literature (8).

The performance characteristics (e.g. turn-on voltage, brightness, and EL quantum efficiency) of the bilayer and single-layer polymer LEDs were found to depend on the intrinsic properties of the materials as well as the "polymer device engineering" factors such as the layer thicknesses and the nature of the polymer/polymer interface. We illustrate some of these results by an example of bilayer PPyBT/PPV LEDs whose EL spectra are shown in Figure 5. It is seen that by varying the relative layer thicknesses of the bilayers the EL spectrum and its voltage dependence vary dramatically. In Figure 5a, a green colored EL was observed when the PPyBT: PPV layer thickness ratio of 6:5 was used. At a ratio of 8:5 the emission color is orange (Figure 5b). Finally at a ratio of 13:5, in Figure 5c we observe a strong voltage dependence of EL spectra in going from a yellow-orange (13V) to a green color (15V). This strong film thickness dependence of emission from bilayer LEDs reflects the variation of charge transport and charge trapping processes in the conjugated polymer films. The EL quantum efficiency and turn-on voltage were observed to also vary with the relative layer theiknesses of the bilayers in Figure 5 and others.

Conclusions

We have successfully fabricated and evaluated bilayer photoreceptors and light-emitting diodes using conjugated rigid-rod polymers as the active materials. The important role of "polymer device engineering" factors on the efficiency for converting charges to light (LEDs) or of light to charges (photoreceptors) was demonstrated. In particular, we have found that the film thickness can significantly influence the performance of these optoelectronic devices. This is a consequence of the charge transport and charge trapping processes in conjugated polymers. The successful development of optoelectronic devices from electronic polymers will therefore require advances of both materials and what we call "polymer device engineering".

Acknowledgments

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Key Word/Phrase Index

Electronic polymers; light-emitting diodes; xerographic photoreceptors; quantum efficiency.

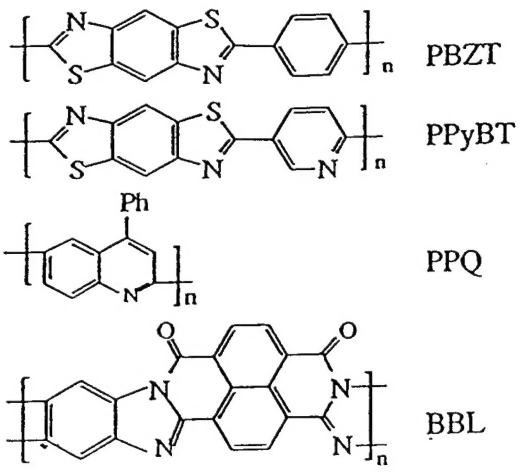

Figure 1. Molecular structure of representative conjugated polymers

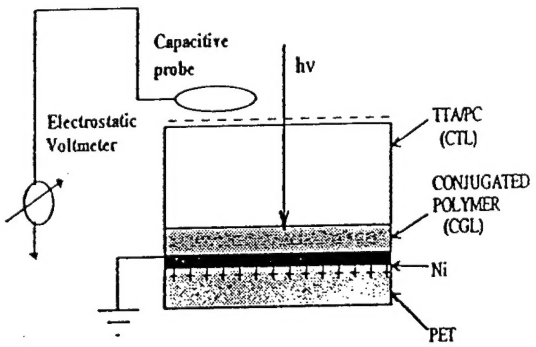

Figure 2. Bilayer photoreceptor devices

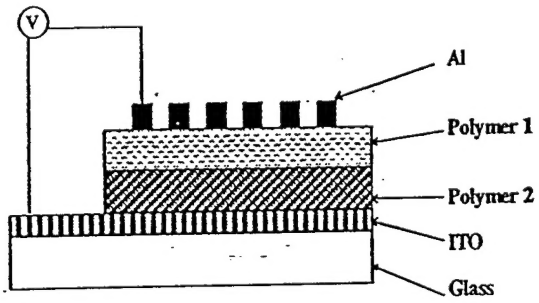

Figure 3. Bilayer light-emitting diode

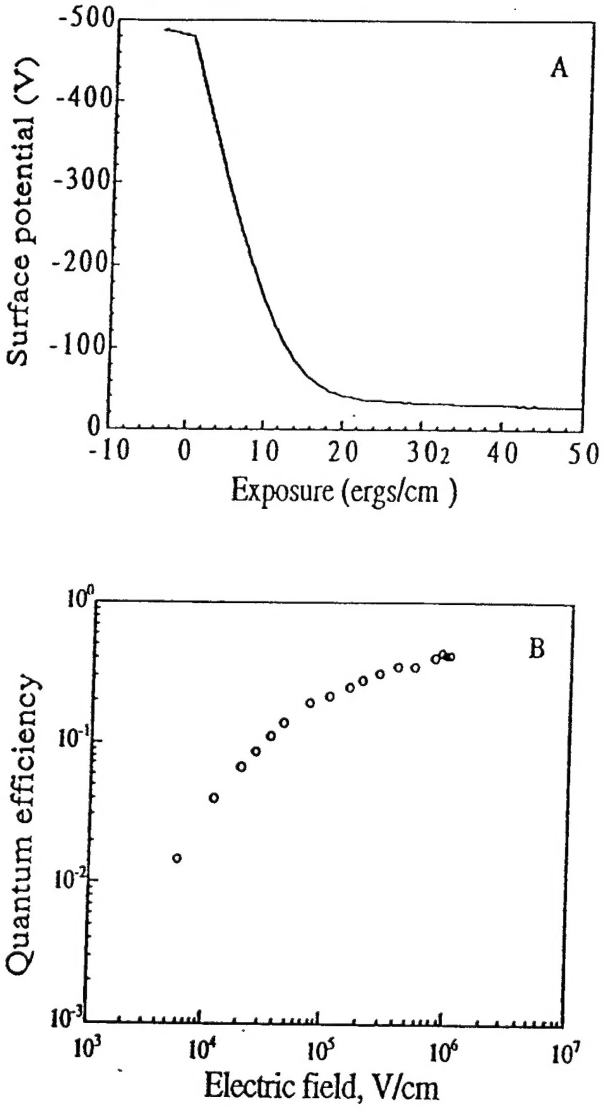

Figure 4. THE PIDC data for a PPyBT/TTA bilayer photoreceptor illuminated at 470 nm (A). The field dependent quantum efficiency (B) of the same photoreceptor as in A.

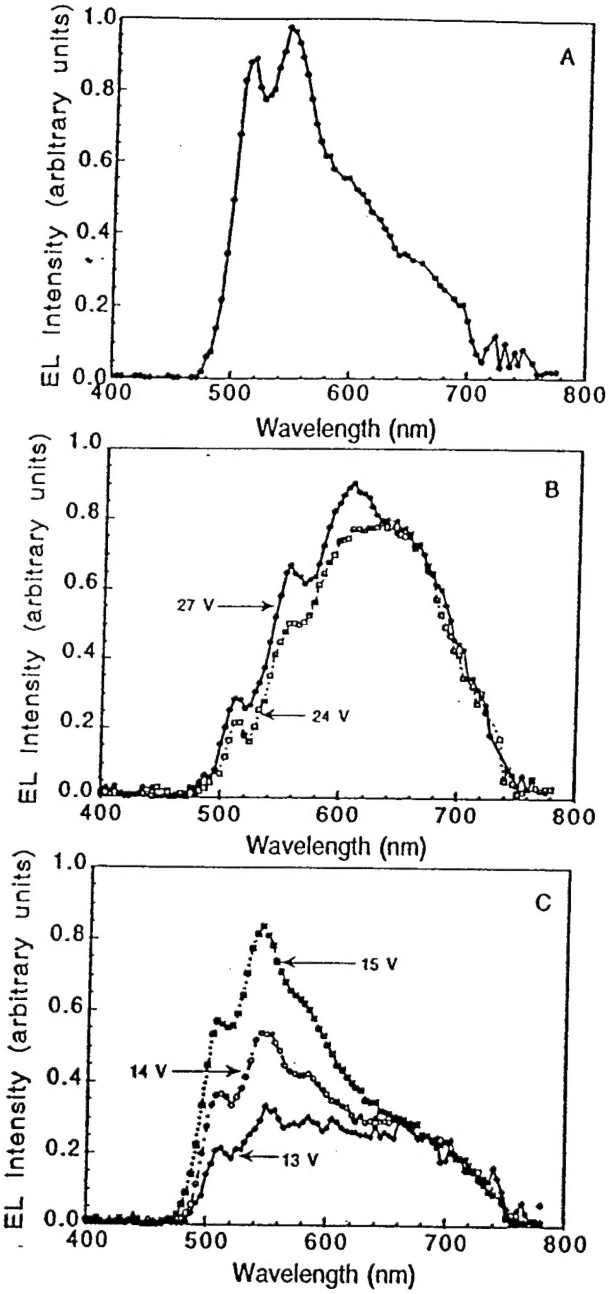

Figure 5. EL spectra of PPyBT/PPV bilayer LEDs. (A) PPyBT:PPV ratio of 6:5; (B) PPyBT:PPV ratio of 8:5; (C) PPyBT:PPV ratio of 13:5.